

Summary Information for New High-hardness Materials Based on AlMgB14

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Background

It has long been accepted that the hardest materials possess strongly bonded crystal structures of high symmetry. Hardness is a function of both the strength of the interatomic bonding and of the rigidity of the lattice framework. Diamond is the hardest known bulk material (approximately 70 GPa), due to strong covalent sp^3 bonding in a tetrahedral lattice configuration. The cF8 structure of diamond is also found in most other ultra-hard materials such as cubic-BN and several of the tetravalent metal carbides.

Recent work at Ames Laboratory has shown unexpectedly high hardness in aluminum magnesium boride combined with 5 to 30 mol.% additives (AlMgB14 + X). Microhardness values were corroborated by measurement using three independent units, one of which was equipped with a state-of-the-art CCD image capture and analysis system. Microhardness measurements on cubic boron nitride and silicon carbide reference samples using these instruments gave excellent agreement with literature values. Matkovich and Economy (1) first reported the orthorhombic AlMgB14 intermetallic compound (oI64, space group Imam, $a=0.5848$ nm, $b=0.8112$ nm, $c=1.0312$ nm.), and the structure determination was later refined by Higashi

and Ito (2). Early work on this material was performed on single crystals; and the present work at Ames Laboratory has been conducted on polycrystalline materials. Very limited mechanical property work was performed on the material prior to the Ames Lab work performed by Bruce Cook, Joel Haringa, and Alan Russell. The table below provides a comparison of the hardness of these new materials, along with several other hard materials and their corresponding density, bulk, and shear moduli (3).

	Density (g/cm ³)	Hardness (GPa)	Bulk Modulus (GPa)	Shear Modulus (GPa)
C (diamond)	3.52	70	443	535
BN (cubic)	3.48	45-50	400	409
C ₃ N ₄ (cubic)	†	40-55	496	332
SiC	3.22	24-28	226	196
Al ₂ O ₃	3.98	21-22	246	162
TiB ₂	4.50	30-33	244	263
WC	15.72	23-30	421	
TiC	4.93	28-29	241	188
AlB ₁₂	2.58	26		
Si ₃ N ₄	3.19	17-21	249	123
AlMgB ₁₄	2.66	32-35*		
AlMgB ₁₄ + X1	2.67	35-40*		
AlMgB ₁₄ + X2	2.70	40-46*		

** hardness values from Ames Lab study*

† presently available in quantities too small to permit measurement of bulk density and hardness

Much of the Ames Lab work performed to date has been devoted to development and optimization of a suitable method for preparing AlMgB₁₄ with no other elements added ("baseline" material) and consolidation of the powder into a dense compact. Processing parameters are now fairly well understood, and the production method has become reliably reproducible.

These AlMgB₁₄-based materials are quite different from other ultra-hard materials in several ways. The conventional paradigm for ultra-hard materials calls for a simple, symmetric, isotropic crystal structure. Moreover, that crystal structure should possess few degrees of freedom within the unit cell to frustrate the material's ability to react to compressive loading by relaxing into another configuration that lowers total system energy. The oI64 structure of baseline AlMgB₁₄ is quite complex; its low symmetry, large number of atoms per unit cell, and, in some specimens, incompletely occupied atom sites all appear to contradict the accepted precepts for extreme hardness. Nevertheless, the baseline material is among the hardest substances known. An additional paradox is introduced by the observation that some additives actually increase the hardness of the material. In most ultra-hard materials, adding additional elements or compounds lowers hardness. Still another apparent departure from the previous paradigm of ultra-hard materials is the good electrical conductivity (1.2 to 7.2(10⁻⁴) Ohm-cm, depending on composition) of these materials, a sharp contrast to the electrically insulating properties of other ultra-hard materials.

Availability of These Materials and Current Status of the Research

Experimental work performed to date has involved relatively small specimens (typically a few grams). Following initial announcement of this discovery, numerous inquiries were received from industry and other research institutions requesting material for testing. Many of the requestors sought to obtain one to two kilogram quantities. Unfortunately, the present inventory of material (about 50 grams total consisting of different compositions and thermal history) is insufficient to meet this demand. These new materials all contain large amounts of boron, a somewhat expensive material, and for that reason, the final product may never be a “low-cost” material. However, it is anticipated that the cost to produce bulk quantities may be a few hundred dollars per pound, which compares favorably with the cost of diamond and cubic BN powders, which can range upwards from \$2000/lb, depending on composition and particle size. The investigators are currently examining methods to scale-up processing of these materials to the 100 to 500 gram level. Completion of the scale-up research is targeted for an April-May 2000 time frame. In addition to the scale-up effort, a study into the role of purity of the precursor materials is underway, with the goal of achieving a significant reduction in cost of the final product through the use of lower purity “technical” grade boron, as opposed to the more expensive “research” grade material. A full array of tribology tests are planned as soon as sufficient quantities of material become available. Fundamental studies, both experimental and theoretical, are also continuing utilizing such tools as scanning and transmission electron microscopy, x-ray diffraction, ultrasonic techniques, and electronic band structure calculations, in order to advance our understanding of the mechanisms that give rise to such extreme hardness in these materials.

Suitability of These Materials for Industrial Applications

Work at Ames Laboratory has tested static reactivity of these materials with steel, stainless steel, and titanium in a vacuum hot press at temperatures up to 1300°C. There was little evidence of interaction between the metals and the boride material. A large U.S. precision milling company tested the baseline material in a severe machining application on ferrous materials that normally require cubic boron nitride. They reported that the new material tolerated the test without fracture, but appeared to wear at a faster rate than CBN tools. Considerably more testing will be required to determine what utility, if any, these new materials will have for applications such as cutting and grinding. A project is planned at Ames Laboratory to determine the feasibility of applying these materials to metal substrates by both thermal spray and laser deposition techniques. However, thermal spray testing will not be possible until the scale-up work has developed processing parameters to produce kilogram quantities of the materials.

Intellectual Property Rights and Licensing of the Technology

Intellectual property rights to this new material are held by the Iowa State University Research Foundation (ISURF), and all licensing inquiries will be negotiated by ISURF. A U.S. patent application for this technology was submitted earlier in 1999 and is now under review.

References

1. V.I. Matkovich and J. Economy, *J. Acta Cryst.* B26, 616 (1970).
2. W. Higashi and T. Ito, *J. Less Comm. Met.* 92, 239 (1983).
3. D.M. Teter, *MRS Bulletin* 23, 22 (1998).